

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 December 2001 (20.12.2001)

PCT -

(10) International Publication Number
WO 01/96471 A2

(51) International Patent Classification⁷: **C08L 59/00**

(21) International Application Number: **PCT/US01/18182**

(22) International Filing Date: **5 June 2001 (05.06.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
09/591,337 9 June 2000 (09.06.2000) US

(71) Applicant: **E.I. DUPONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).**

(72) Inventors: **MORI, Hiroshi; Utsunomiya-shi, Toyosatodai 2-15-3, Tochigi 321-0964 (JP). SHINOHARA, Kenichi; Utsunomiya-shi, Toyosatodai 2-15-3, Tochigi 320-0003 (JP). FLEXMAN, Edmund, A.; 10 Crestfield Road, Wilmington, DE 19810 (US).**

(74) Agent: **LANGWORTHY, John, A.; E.I. Dupont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).**

(81) Designated States (*national*): AE, AG, AI, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CI, CG, CL, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

-- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **TOUGHENED POLYACETAL RESIN COMPOSITION**

(57) Abstract: A toughened polyacetal resin composition, and a process for making same, is provided by mixing a polyacetal masterbatch component, prepared from polyacetal and a relatively large amount of polyurethane, with a polyacetal dilution component so as to generate a blended composition in which the content of the thermoplastic polyurethane is about 1 to about 15 wt% of the total weight of the blended composition.

WO 01/96471 A2

TITLE

Toughened Polyacetal Resin Composition

Field of the Invention

5 This invention relates to a blended composition containing polyacetal resin (also referred to herein as polyoxymethylene), which composition displays a toughness superior to that of polyacetal but does not sacrifice the other desirable properties that are inherent to a polyacetal resin. More
10 particularly, this invention provides a polyacetal resin composition comprising a small amount of a thermoplastic polyurethane, which composition is manufactured by preparing a polyacetal masterbatch component in which a thermoplastic polyurethane is present at a proportionately high level of content, followed by blending this
15 masterbatch component with further polyacetal resin to dilute the proportionate amount of polyurethane in the final blended composition to the desired level.

Background of the Invention

20 Polyacetal resin, which is prepared by polymerizing a starting material such as formaldehyde monomer or trioxane (which is a trimer of formaldehyde) exhibits excellent mechanical and physical properties, such as tensile strength, stiffness, fatigue resistance, sliding resistance, chemical resistance, and the like.
25 Comonomers may also be present. It is extensively used in mechanical parts, electronic parts, automotive parts, and the like. For certain molded articles, however, obtained by molding a conventional composition containing essentially only polyacetal resin, it would be desirable to have greater toughness than has
30 heretofore been possible with such conventional compositions.

Improving the toughness of a composition of a polyacetal resin has previously required the addition of substantial amounts of toughening agent(s) into the composition. The addition of a substantial amount of toughening agent(s) into a polyacetal composition has often been disfavored, however, since the stiffness and moldability of the composition will be adversely affected, thereby making molding difficult, and disadvantageous effects on operativity and manufacturing costs will also result.

Many technologies related to the improvement of impact resistance by the addition of a variety of additives into a polyacetal resin composition have been known. For example, the prior art technologies for improving impact resistance involve blending a toughening agent, such as polyurethane, into polyoxymethylene [Japanese laid-open patent No. 59 (84)-155452, Japanese laid-open patent No. 59 (84)-155453 and Japanese laid-open patent No. 61 (86)-19652].

U.S. Patent No. 5,286,807 discloses polyoxymethylene compositions having 5 – 15 wt% thermoplastic polyurethane which has a soft segment glass transition of lower than 0 °C and is dispersed in the polyoxymethylene as discrete particles in order to achieve extraordinary impact resistance as measured by Gardner impact.

U.S. Patent No. 4, 804,716 discloses polyoxymethylene compositions having 15 – 40 wt% thermoplastic polyurethane which has a soft segment glass transition of lower than -15°C and is dispersed in the polyoxymethylene as discrete particles in order to

achieve extraordinary impact resistance as measured by Gardner impact.

Japanese laid-open patent No. 4-198355 discloses a
5 polyoxymethylene resin composition comprising 100 wt%
polyoxymethylene resin and 1 –150 wt% thermoplastic polyurethane
to provide molded articles having excellent impact resistance and
mechanical properties and good in surface appearance and heat
aging resistance.

10

Japanese laid-open patent No. 7-207115 discloses a
polyacetal resin composition comprising a thermoplastic elastomer,
preferably a polyurethane or a polyolefin elastomer having 1 – 3000
kg/cm² elastic modulus, which is dispersed in the form of particles
15 with average distance between the particles being given by a
specified formula in order to improve impact resistance.

Japanese laid-open patent No. 5-262957 discloses a
polyacetal resin composition comprising 99-40 wt% polyacetal, 1 –
20 60 wt% polyester type thermoplastic polyurethane elastomer and
0.01 –10 wt% polyhydric alcohol having 3 hydroxyl group in the
molecule, and being prepared by melt-mixing these components at a
temperature in the range of 180 to 250°C under shearing condition.

25 Despite the introduction in the art of the compositions
described above, there is still a demand for means to improve the
toughness of polyacetal in a composition without adversely affecting
the other inherent properties of the polyacetal resin. When
preparing a blended composition from polyacetal and polyurethane,
30 it would also be desirable to do so in a manner that suppresses

any significant degradation of the polyurethane, and any polyacetal yellowing, resulting from the presence of the polyurethane at the higher temperatures encountered during processing and molding.

5 An extensive study by the present inventors has led to the blended composition of this invention, in which greater toughness is obtained than is characteristic of polyacetal alone, but in which there is no offsetting reduction of the other desirable properties that are inherent to the polyacetal resin.

10

Summary of the Invention

In one aspect, this invention involves a blended composition comprising in admixture (a) a polyacetal masterbatch component, and (b) a polyacetal dilution component.

15

In another aspect this invention involves a process for making a blended composition comprising the steps of (a) preparing a polyacetal masterbatch component from a polyacetal resin and a thermoplastic polyurethane, (b) admixing the polyacetal masterbatch component with a polyacetal dilution component, and
20 (c) recovering a blended composition.

In yet another aspect, this invention involves a toughened composition comprising (a) a polyacetal resin, and (b) a
25 thermoplastic polyurethane containing a soft segment having a glass transition temperature of less than -30°C , wherein

(i) said toughened composition is prepared by mixing a polyacetal masterbatch component with a polyacetal dilution component,

(ii) said polyacetal masterbatch component is prepared by mixing a polyacetal resin with a thermoplastic polyurethane, said thermoplastic polyurethane being about 10 to about 60 wt% of the masterbatch component, and

5 (iii) said toughened composition has a total thermoplastic polyurethane content of about 1 to about 15 wt%.

In a further aspect, this invention involves an article of manufacture prepared from the blended composition of this invention.

Detailed Description of the Invention

The blended composition of this invention is prepared by admixing a polyacetal masterbatch component with a polyacetal dilution component. The polyacetal masterbatch component is prepared by admixing a polyacetal resin and a polyurethane, preferably a thermoplastic polyurethane. The polyacetal dilution component is a polyacetal resin. The content of polyurethane is substantially higher in the polyacetal masterbatch component than it is in the final blended composition. The polyacetal dilution component is thus used to dilute the relative content of the polyurethane down from the higher level characteristic of the masterbatch component to a lower level as desired in the final blended composition. The process of this invention involves the preparation of a blended composition in the manner described above.

Polyacetal resin, which is used herein to make the polyacetal masterbatch component and as the polyacetal dilution

component, includes homopolymers of formaldehyde or of cyclic oligomers of formaldehyde, the terminal groups of which are end-capped by esterification or etherification; and also includes copolymers of formaldehyde or of cyclic oligomers of formaldehyde and other monomers that yield oxyalkylene groups with at least two adjacent carbon atoms in the main chain, the terminal groups of which copolymers can be hydroxyl terminated or can be end-capped by esterification or etherification.

10 The polyacetal used in the composition of the present invention can be branched or linear, with terminal groups thereof being either not protected or being protected. The polyacetal resin will generally have a number average molecular weight in the range of about 10,000 to about 100,000, preferably about 20,000 to about 15 70,000, and more preferably about 35,000 to about 70,000. The molecular weight can conveniently be measured by gel permeation chromatography in *m*-cresol at 160°C using a Du Pont PSM bimodal column kit with nominal pore size of 60 and 1000 Angstrom.

20 As indicated above, the polyacetal used in the present invention can be either a homopolymer, a copolymer, or a mixture thereof. Copolymers can contain one or more comonomers, such as those generally used in preparing polyacetal compositions. Comonomers more commonly used include alkylene oxides of 2-12 25 carbon atoms and their cyclic addition products with formaldehyde. The quantity of comonomer will not be more than 20 weight percent, preferably not more than 15 weight percent, and more preferably about 2 weight percent. The most preferred comonomer is ethylene oxide. Generally, polyacetal homopolymer is preferred 30 over copolymer because of its greater stiffness. Preferred polyacetal

homopolymers include those on which terminal hydroxyl groups have been end-capped by a chemical reaction to form ester or ether groups, preferably acetate or methoxy groups, respectively.

5 The polyurethane useful in the present invention is prepared by reacting a polymeric soft segment precursor having at least two hydroxyl groups per molecule (a "polyol") and having a molecular weight of at least about 500, preferably from about 550 to about 5,000, and more preferably from about 1,000 to about 2,500,
10 such as a dihydric polyester or a polyalkylene ether diol. The polyol is reacted with an organic diisocyanate in a ratio such that a substantially linear polyurethane polymer results, although some branching can be present. A diol chain extender having a molecular weight less than about 250 may also be incorporated.
15 The mole ratio of isocyanate to hydroxyl in the polymer is preferably from about 0.95 to 1.08, more preferably 0.95 to 1.05, and most preferably, 0.95 to 1.02. In addition, monofunctional isocyanates or alcohols can be used to control molecular weight of the polyurethane.

20

Suitable polyester polyols include the polyesterification products of one or more dihydric alcohols with one or more dicarboxylic acids. Suitable dicarboxylic acids include adipic acid, succine acid, sebacic acid, pimelic acid, azelaic acid, thiodipropionic
25 acid and citraconic acid and mixtures thereof including small amounts of aromatic dicarboxylic acids. Suitable dihydric alcohols include ethylene glycol, 1,3- or 1,2-propylene glycol, 1,4-butanediol, 1,3-butanediol, 2-methyl pentane diol-1, 5, diethylene glycol, 1,5-pentanediol, 1,6-hexanediol, 1,12-dodecanediol and mixtures
30 thereof. Further, hydroxycarboxylic acids, lactones and cyclic

carbonates, such as ϵ -caprolactone and 3-hydroxybutyric acid can be used in the preparation of the polyester. Preferred polyesters for use as a polyol include poly (ethylene adipate), poly (1,4-buthylene adipate), mixtures of these adipates and poly ϵ -caprolactone.

5

Suitable polyether polyols include the condensation products of one or more alkylene oxides with a small amount of one or more compounds having active hydrogen-containing groups, such as water, ethylene glycol, 1,2- or 1,3-propylene glycol, 1,4-
10 butanediol and 1,5-pentanediol, and mixtures thereof. Suitable alkylene oxide condensates include those of ethylene oxide, 1,2-propylene oxide and butylene oxide and mixtures thereof. Suitable polyalkylene ether glycols may also be prepared from tetrahydrofuran. In addition, suitable polyether polyols can
15 contain comonomers, especially as random or block comonomers, such as ether glycols derived from ethylene oxide, propylene oxide and/or tetrahydrofuran (THF). Alternatively, a THF polyether copolymer with minor amounts of 3-methyl THF can also be used.

20 Preferred polyethers for use as a polyol include poly (tetramethylene ether) glycol (PTMEG), poly (propylene oxide) glycol, copolymers of propylene oxide and ethylene oxide, and copolymers of tetrahydrofuran and ethylene oxide. Other suitable polymeric diols include those, which are primarily hydrocarbon in nature, e.g.,
25 polybutadiene diol.

Suitable organic diisocyanates include 1,4-butylene diisocyanate; 1,6-hexamethylene diisocyanate; cyclopentylene-1,3-
diisocyanate; 4,4"-dicyclohexymethane diisocyanate; 2,4-tolyene
30 diisocyanate; 2,6-tolyene diisocyanate; isomeric mixtures of 2,4-

and 2,6-tolylene diisocyanate; 4,4"-methylene bis
(phenylisocyanate); 2,2-diphenylpropane-4,4"-diisocyanate; p-
phenylene diisocyanate; m-phenylene diisocyanate; xylylene
diisocyanate; 1,4-naphthylene diisocyanate; 1,5-naphthylene
5 diisocyanate; 4,4"-diphenyl diisocyanate; azobenzene-4,4"-
diisocyanate; m- or p-tetramethylene diisocyanate; 1-
chlorobenzene-2,4-diisocyanate. 4,4"-methylene
bis(phenylisocyanate); 1,6-hexamethylene diisocyanate; 4,4"-
dicyclohexylmethane diisocyanate and 2,4-tolylene diisocyanate are
10 preferred.

Secondary amide linkages including those derived from
adipyl chloride and piperazine, and secondary urethane linkages
including those derived from the bis-chloroformates of PTMEG
15 and/or butanediol, can also be introduced into the polyurethane.

Dihydric alcohols suitable for use as chain extending
agents in the preparation of the thermoplastic polyurethanes
include those containing carbon chains which are either
20 uninterrupted, or which are interrupted by oxygen or sulfur
linkages, including 1,2-ethanediol; 1,2-propanediol; isopropyl-a-
glyceryl ether; 1,3-propanediol; 1,3-butanediol; 2,2-dimethyl-1,3-
propanediol; 2,2-diethyl-1,3-propanediol; 2-ethyl-2butyl-1,3-
propanediol; 2-methyl-2,4-pentanediol; 2,2,4-trimethyl-1,3-
25 pentanediol; 2-ethyl-1,3-hexanediol; 1,4-butanediol; 2,5-
hexanediol; 1,5-pentanediol; dihydroxy-cyclopentane; 1,6-
hexanediol; 1,4-cyclohexanediol; 4,4"-cyclohexanedimethylol;
thiodiglycol; diethyleneglycol; dipropylene glycol; 2-methyl-1,3-
propanediol; 2-methyl-2-ethyl-1,3-propanediol; dihydroxyethyl
30 ether of hydroquinone; hydrogenated bisphenol A; dihydroxy-ethyl

terephthalate and dihydroxymethyl benzene, and mixtures thereof. Hydroxyl terminated oligomers of 1,4-butanediol terephthalate can also be used, giving a polyester-urethane-polyester repeating structure. Diamines can also be used as chain extending agents
5 giving urea linkages. 1,4-Butanediol, 1,2-ethanediol and 1,6-hexanediol are preferred.

In the preparation of a thermoplastic polyurethane, the ratio of isocyanate to hydroxyl should be close to unity, and the
10 reaction can be a one step reaction. The polyurethane used in the composition of this invention typically has a soft segment, *i.e.* that formed as a result of the incorporation of the polyol, having a glass transition temperature of less than about -30°C.

15 With the polyacetal blended composition of this invention, one may intermix known additives conventionally used in engineering resins to obtain desired properties. These optional additives include, for example, lubricants, nucleating agents, mold release agents, antistatic agents, surfactants, organic polymeric
20 materials; and inorganic or organic, fibrous, granular or plate-like fillers. These additives can be used either alone or in combinations of two or more, at a level of content that does not negate the effects of this invention.

25 Representative lubricants that may be used for the polyacetal compositions of this invention include, but are not limited to, silicones such as dimethylpolysiloxanes and their modifications; oleic acid amides; erucic acid amides; stearic acid amides; bis-fatty acid amides such as bisamides; non-inonic
30 surfactants; hydrocarbon waxes; chlorohydrocarbons;

fluorocarbons; fatty acids including oxy-fatty acid; esters including lower alcohol esters of fatty acids; alcohols including polyvalents, polyglycols, polyglycerols; and metal soaps such as lauric acid or stearic acid, and the like, with metals.

5

Also, it is desirable to add an antioxidant to prevent thermal deterioration of the resin and to suppress the formation of fish-eyes and lumps (non-homogeneous lump breakdown). Hindered phenol type antioxidants are most preferred in this invention. Those antioxidants with a melting point higher than 100°C, especially above 120°C, are most preferred.

It is also desirable to add heat stabilizers to the composition of this invention. These include polyamide compounds, especially nylon terpolymers, hydroxy containing polymers, and nonmelting nitrogen or hydroxy containing compounds, *e.g.* polyamide 6, polyamide 6/12 copolymer, polyamide 6/66/610 terpolymer, polyamide 6/66/612 terpolymer, ethylene-vinyl alcohol copolymer, acrylamide (co)polymer, acrylamide/N,N-methylenebis-acrylamide copolymer.

To prepare the composition of the present invention, a polyurethane is first compounded with a polyacetal, and is then melt mixed and extruded to prepare the polyacetal masterbatch component. The amount of polyurethane used for incorporation into the polyacetal masterbatch component should be adjusted so that when the polyacetal masterbatch component is admixed with the polyacetal dilution component, the resultant blended composition has a final polyurethane content within the range of about 1 to about 15 wt%, although lower amounts such as about 1

to about 10 wt%, about 1 to about 5 wt%, about 1 to less than 5 wt%, or about 1 to about 4 wt% also give the desired result. A total polyurethane content in a range as described above, in the blended composition formed from the mixture of the polyacetal masterbatch component and the polyacetal dilution component, achieves an excellent balance of both impact resistance and the other inherent and desirable properties of a polyacetal resin.

A polyurethane content in the final blended composition as described above can be obtained by preparing the polyacetal masterbatch component from the ingredients in a ratio of about 40 to about 90 wt% polyacetal, and about 10 to about 60 wt% polyurethane; preferably about 60 to about 75 wt% polyacetal and about 25 to about 40 wt% polyurethane. Once the polyacetal masterbatch component has been prepared, it is typically combined with the polyacetal dilution component in a ratio of about 5 to about 60 wt% masterbatch component and about 40 to about 95 wt% dilution component; preferably about 10 to about 40 wt% masterbatch component, and about 60 to about 90 wt% dilution component. As a result of the preparation of the blended composition of this invention, the polyurethane becomes dispersed in a matrix of the polyacetal as particles having a size in the range of about 0.2 to about 5 microns.

The toughened polyacetal blended composition of this invention can be manufactured by any well-known manufacturing method. For example, by using an extruder, either or both of the polyacetal masterbatch component and the polyacetal dilution component may be added as a dry powder, as a concentrate, as a dispersion, or as a solution; and may be simultaneously blended,

melted and extruded together within the extruder. In addition, the preparation of the polyacetal masterbatch component from a polyacetal and a polyurethane, and the subsequent compounding of the masterbatch component with the polyacetal dilution component, may occur as appropriately timed and staged sequences in the same mixer. Moreover, a pellet made from the masterbatch component and a pellet made from the dilution component may also be mixed and supplied to a molding machine for the manufacture of a molded article. Furthermore, in a molding machine with the installation of an appropriate screw, the polyacetal masterbatch component and the polyacetal dilution component may be supplied directly for the manufacture of a molded article.

The process of this invention involves the preparation of a blended composition in the manner described above.

An article of manufacture such as a molded part may be prepared from the polyacetal blended composition of this invention. Any molding process conventional in the plastics-forming art including, for example, compression molding, vacuum forming, injection molding, extrusion molding, blow molding, rotary molding, melt spinning, and heat molding may be used. Especially preferred for obtaining parts pertaining to the composition of this invention is injection molding. For example, gears, buckles and toy parts may be made from the composition of this invention. A process of molding the composition of this invention, as described above, may be combined with a process of making the composition of this invention, as described above.

Examples

The present invention and its advantageous technical effect is described by tests performed on sample materials. The examples of the invention (Examples 1-5) are contrasted against various controlled formulations (Controls A-E) that do not possess the properties of the composition of this invention. The examples are presented for the purpose of explaining the present invention, and should not be understood as a limitation on the scope of this invention.

10

Test methods:

In the examples and controls, the characteristics of the polyacetal blended compositions, and the molded articles prepared therefrom, were determined by the following test methods:

15

Impact resistance was measured according to ISO 179/1eA (Charpy Impact). Each sample was injection molded as a tensile bar in accordance with ISO 3167, and the bars were allowed to stand at room temperature (approximately 25°C) at least one week after molding prior to testing.

20

Flexural modulus was determined in accordance with ISO 178. Each sample was injection molded as a tensile bar in accordance with ISO 3167, and the bars were allowed to stand at room temperature at least one week after molding prior to testing.

25

Elongation was determined in accordance with ISO 527-1/-2. Each sample was injection molded as a tensile bar in

accordance with ISO 3167, and the bars were allowed to stand at room temperature at least one week after molding prior to testing.

5 Components:

 The polyacetal resins used in the examples and controls were Delrin®500 capped polymer (hereafter CP500), and Delrin®100 capped polymer (hereafter CP100), which are both polyacetal homopolymers made by E.I. du Pont de Nemours and
10 Company of Wilmington, Delaware. A thermoplastic polyurethane, such as described in US 4,804,716, was used as the polyurethane (hereafter TPU) from which the polyacetal masterbatch component was prepared.

15

Preparations:

 70 wt% of CP100 is mixed with 30 wt% of TPU in an extruder (a Toshiba twin screw extruder) at 220°C and 310 rpm, and the resultant resin is pelletized to prepare pellets of the
20 masterbatch component. The resulting masterbatch pellets are mixed and diluted with CP500 to obtain a blended composition in which polyurethane is present at much lower content level than 30 wt%. The level of content of polyurethane in the blended composition obtained in Examples 1-5 is shown in Table 1
25 Controls A-E were those obtained by adding polyurethane at the same level of content as in the blended composition of each of the examples but without prior preparation of a masterbatch component before addition of the polyacetal dilution component.

The results of evaluation are listed in Table 2, and demonstrate that, when a blended composition is prepared by first preparing a polyacetal masterbatch component before mixing with a polyacetal dilution component, a blended composition is obtained in
5 which the impact resistance is improved while at the same time preserving good balance with the other inherent and desirable properties of a polyacetal resin.

Table 1

Sample	Wt. % Masterbatch	Wt. % CP100	Wt. % TPU	Wt. % CP500	Net Wt. % TPU
Example 1	5.0	-	-	95.0	1.5
Control A	-	3.5	1.5	95.0	1.5
Example 2	10.0	-	-	90.0	3
Control B	-	7.0	3.0	90.0	3
Example 3	15.0	-	-	85.0	4.5
Control C	-	10.5	4.5	85.0	4.5
Example 4	20.0	-	-	80.0	6
Control D	-	14.0	6.0	80.0	6
Example 5	33.3	-	-	66.7	10
Control E	-	23.3	10.0	66.7	10

5

Table 2

Sample	Notched Charpy Impact (KJ/m ²)	Flexural Modulus (MPa)	Elongation (%)
Example 1	9.43	3017	38.00
Control A	9.28	3005	27.15
Example 2	10.02	2896	50.55
Control B	9.88	2883	27.95
Example 3	12.52	2737	42.35
Control C	11.27	2774	26.00
Example 4	13.69	2617	40.45
Control D	10.89	2677	26.85
Example 5	14.91	2343	38.50
Control E	11.91	2413	32.15

What is claimed is:

1. A toughened composition comprising (a) a polyacetal resin, and (b) a thermoplastic polyurethane containing a soft
5 segment having a glass transition temperature of less than -30°C ,
wherein

(i) said toughened composition is prepared by mixing a polyacetal masterbatch component with a polyacetal dilution component,

10 (ii) said polyacetal masterbatch component is prepared by mixing a polyacetal resin with a thermoplastic polyurethane, said thermoplastic polyurethane being about 10 to about 60 wt% of the masterbatch component, and

(iii) said toughened composition has a total
15 thermoplastic polyurethane content of about 1 to about 15 wt%.

2. A composition according to Claim 1 wherein the polyacetal resin utilized in the polyacetal masterbatch component or
20 as the polyacetal dilution component is a homopolymer.

3. A composition according to Claim 1 wherein the polyacetal resin utilized in the polyacetal masterbatch component as the polyacetal dilution component is an acetal copolymer.

25

4. A composition according to Claim 3 wherein the acetal copolymer is prepared from formaldehyde and ethylene oxide.

5. A composition according to Claim 1 wherein the polyurethane is dispersed in the polyacetal as particles having a size of about 0.2 to about 5 microns.

5 6. A composition according to Claim 1 further comprising one or more additives selected from the group consisting of stabilizers, impact modifiers, reinforcing agents, antistatic agents, antioxidants, plasticizers, lubricants, fillers and colorants.

10 7. A composition according to Claim 1 in the form of an article of manufacture.

 8. A process for making a blended composition comprising (a) preparing a polyacetal masterbatch component from
15 a polyacetal resin and a thermoplastic polyurethane, (b) admixing the polyacetal masterbatch component with a polyacetal dilution component, and (c) recovering a blended composition.

 9. A process according to Claim 8 wherein the
20 polyurethane content within the blended composition is about 1 to about 15 weight percent.

 10. A process according to Claim 8 wherein the polyacetal resin utilized in the polyacetal masterbatch component or
25 as the polyacetal dilution component is a homopolymer or a copolymer.

11. A process according to Claim 8 wherein the polyurethane contained in the polyacetal masterbatch component has a soft segment glass transition temperature of less than about -30°C.

5

12. A process according to Claim 8 wherein the polyurethane is dispersed in the polyacetal as particles having a size of about 0.2 to about 5 microns.

10

13. A process according to Claim 8 wherein step (b) comprises a step of admixing the polyacetal masterbatch component with a polyacetal dilution component and one or more additives selected from the group consisting of stabilizers, impact modifiers, reinforcing agents, antistatic agents, antioxidants, plasticizers, lubricants, fillers and colorants.

15

14. A blended composition comprising in admixture (a) a polyacetal masterbatch component, and (b) a polyacetal dilution component.

20

15. A composition according to Claim 14 wherein the polyurethane content within the blended composition is about 1 to about 15 weight percent.

25

16. A composition according to Claim 14 wherein the polyurethane content within the blended composition is about 1 to less than 5 weight percent.

17. A composition according to Claim 14 wherein the polyacetal resin utilized in the polyacetal masterbatch component or as the polyacetal dilution component is a homopolymer or a copolymer.

5

18. A composition according to Claim 14 wherein the polyurethane contained in the polyacetal masterbatch component has a soft segment glass transition temperature of less than about -30°C.

10

19. A composition according to Claim 14 wherein the polyurethane is dispersed in the polyacetal as particles having a size of about 0.2 to about 5 microns.

15

20. A composition according to Claim 14 further comprising one or more additives selected from the group consisting of stabilizers, impact modifiers, reinforcing agents, antistatic agents, antioxidants, plasticizers, lubricants, fillers and colorants.

20

21. A composition according to any one of Claims 14~20 in the form of an article of manufacture.

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 December 2001 (20.12.2001)

PCT

(10) International Publication Number
WO 01/96471 A3

(51) International Patent Classification⁷: C08L 59/00

(21) International Application Number: PCT/US01/18182

(22) International Filing Date: 5 June 2001 (05.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/591,337 9 June 2000 (09.06.2000) US

(71) Applicant: E.I. DUPONT DE NEMOURS AND COMPANY [US/US]: 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors: MORI, Hiroshi; Utsunomiya-shi, Toyosatodai 2-15-3, Tochigi 321-0964 (JP). SHINOHARA, Kenichi; Utsunomiya-shi, Toyosatodai 2-15-3, Tochigi 320-0003 (JP). FLEXMAN, Edmund, A.; 10 Crestfield Road, Wilmington, DE 19810 (US).

(74) Agent: LANGWORTHY, John, A.; E.I. Dupont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(81) Designated States (*national*): AF, AG, AI, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW). Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR). OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:
2 May 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TOUGHENED POLYACETAL RESIN COMPOSITION

(57) Abstract: A toughened polyacetal resin composition, and a process for making same, is provided by mixing a polyacetal masterbatch component, prepared from polyacetal and a relatively large amount of polyurethane, with a polyacetal dilution component so as to generate a blended composition in which the content of the thermoplastic polyurethane is about 1 to about 15 wt% of the total weight of the blended composition.



WO 01/96471 A3

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 01/18182

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L59/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 290 761 A (DEGUSSA) 17 November 1988 (1988-11-17) page 5, line 46 -page 6, line 39; claim; tables 1,3	1-3,6,7
A	EP 0 121 407 A (DU PONT) 10 October 1984 (1984-10-10) page 1, line 10 - line 25; claims 1,5,13; example 1 page 19, line 25 - line 37	1-7
A	US 4 707 525 A (LANIEVE III H LESLIE ET AL) 17 November 1987 (1987-11-17) column 6, line 14 - line 22; claims 1,2,6; examples 1,2,7 & JP 61 019652 A 28 January 1986 (1986-01-28) cited in the application	1-4,6,7

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

28 February 2002

Date of mailing of the international search report

08/03/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Angiolini, D

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/18182

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0290761	A	17-11-1988	DE 3714267 A1	10-11-1988
			EP 0290761 A2	17-11-1988
			JP 63280758 A	17-11-1988
EP 0121407	A	10-10-1984	EP 0121407 A2	10-10-1984
			JP 59196357 A	07-11-1984
US 4707525	A	17-11-1987	CA 1234947 A1	05-04-1988
			DE 3574718 D1	18-01-1990
			EP 0167369 A1	08-01-1986
			JP 1750990 C	08-04-1993
			JP 4039498 B	29-06-1992
			JP 61019652 A	28-01-1986

THIS PAGE BLANK (USPTO